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ON THE POSSIBILITY OF MULTI-PHONON EXCITATION OF INTERNAL MOLECULAR VIBRATIONS AS THE RATE CONTROLLING PROCESS IN SHOCK INITIATION

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The possibility that the rate controlling process in shock-induced bond breaking in energetic materials is a transfer of lattice phonons to internal vibrations of the molecules of the explosive solid is examined. The rate at which three lattice phonons can excite an internal vibrational mode of the molecules of the lattice is estimated. This is then used to calculate the mean time for a molecule to be excited to a state having energy equal to the dissociation energy of the molecular bond, assuming no transfer of energy to other vibrational modes of the molecule and assuming a truncated harmonic oscillator

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form for the potential. It is noted that bonds that can not break at atmospheric pressure may be susceptible to unimolecular breaking at higher pressures, indicating that the reactions of slow thermal decomposition may not necessarily be the important reactions of shock induced bond breaking.

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INTRODUCTION

Although it has been long known that certain organic and inorganic solids, when subjected to shock pulses undergo rapid exothermic reaction, there is little understanding of the process on the atomic or molecular level. Since the phenomena has wide military and civilian application a fundamental understanding of the process should have an important impact on the technology. A determination of the relationship between the molecular or atomic parameters such as electronic structure and vibrational properties of the system and the macroscopic behavior, such as explosive yields and sensitivity should enable more precise control of the conditions which influence the start of reaction.

The process of bond breaking in a molecule of an explosive solid may start in the solid state. Certainly in primary explosives, such as PbN_6 and TlN_3, there is little doubt that the low shock pulses required to cause detonation (less than 10 Kb) can not raise the temperature of the explosive to be in excess of the melting temperature. This is probably even true in inhomogeneous primary explosives.

Only very recently has there been some experimental effort to understand the process on the molecular level. Solid explosives which were subjected to shocks of pulse height and width less than necessary to cause detonation were examined by a number of microscopic experimental techniques. These experiments indicate that the shock pulses break intra-molecular bonds of the constituent molecules of the solids (refs. 1, 2). In some cases, the bonds broken by shock were not the same as the dominant bonds severed by slow thermal decomposition studies. In RDX the major product of the shock decomposition is NO_2 which is a minor product in thermal decomposition (ref. 3). There is other evidence to indicate that the reactions leading to rapid exothermic reaction are not the same as the dominant reactions of slow thermal decomposition. The rates of reaction calculated from slow thermal decomposition studies of solid explosives at the initiation temperature are far too low to explain explosion.

If the process of bond breaking in a shock compressed solid is a unimolecular thermal process, the rate controlling step will be the rate at which lattice energy (heat) generated by the shock pulse is transferred to the internal vibrational modes of the molecules which make up the lattice of the explosive solid. It is necessary that the relaxation time for this process be at least in the order of magnitude of the pulse width of the shock (10^{-6} S). Because of this, it is possible that bonds broken in slow thermal decomposition studies may not be broken in pulsed decomposition. It is also possible that the effect of lattice compression may influence the particular bonds that are broken.

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The purpose of this work is to investigate whether unimolecular bond breaking due to shock heating can occur in a shock compressed solid, and to examine why different bonds can be broken in shock compressed lattices than in slow heated lattices. The rate at which lattice energy is transferred to specific internal bonds of the molecules of the lattice will be estimated and the rate at which these bonds can be broken, will be calculated. The effect of shock compression on this process will be considered. The approach is to adapt an existing model, the Montroll-Shuler model, for the transfer of energy to a molecule from a thermal bath to a situation where the bath, the crystal lattice, is subject to shock compression. Once the rate of transfer of energy is determined, and thus the probability for internal vibrational excitation of the molecule, the rate at which a unimolecular breaking of the bond can occur is calcuated from random walk theory.

THEORY

Those explosives in which the initial chemical processes start in the solid state are considered. This represents a reasonably wide class of energetic materials. Certainly in the primary explosives such as the azides or fulminates which are initiated with shock pulses less than 10 Kb in peak pulse pressure, the initial reaction induced by the shock pulse occur in the solid state. A shock pulse of less than 10 Kb causes a temperature rise of only a few degrees. In the secondary solid explosives recent experiments which allow an estimation of the rate of shock induced reaction as a function of peak pulse pressure and shock temperature, indicate that the reaction can occur at shock temperatures well below the melting temperatures of the explosives (ref. 4).

In order to examine the possibility that the temperature rise due to a shock pulse applied to a solid can cause a unimolecular breaking of the intra-molecular bonds of the constituent molecules or molecular ions of the solid, the Montroll-Shuler model (ref. 5), for dissociation of a molecule immersed in a thermal bath, the lattice of the solid, is adapted to the case where the solid is shock compressed. The idea of the model, is that the shock wave heats the lattice exciting higher vibrational states of the normal modes of vibration of the lattice. Because there may exist a coupling between the external modes of the lattice and the internal modes of the molecules which make up the lattice, some number of lattice phonons may be transferred to an internal mode of the molecule causing an excitation to the first vibrational state. Unimolecular bond breaking occurs if there is some probability that the vibration associated with the bond can be excited to a state $N = L$ which has energy equal to or greater than

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the dissociation energy of the bond, i.e., $D_e = (L + 1)$ hν. The reaction rate on this model is then the reciprocal of the mean time needed for the molecule to be excited from state $N = 0$ to state $N = L$. A most likely possibility is that the process be a three phonon process because typically, three lattice phonons will be in the order of the energy separation between the vibrational states of the molecule. The probability per unit time for this three phonon process is given by,

$$W_{10} = \frac{1}{t} \int\int \quad P_{if} \; g(\omega_1) \; g(\omega_2) \; g(\omega_3) \; d\omega_1 d\omega_2 d\omega_3. \tag{1}$$

where $\omega_1, \omega_2, \omega_3$, are the frequencies of the lattice modes. $g(\omega_1)$, $g(\omega_2)$, and $g(\omega_3)$ are the density of final phonon states. The P_{if} is

$$P_{if} = \frac{2\pi t}{\hbar^2} \; \left| \; < f | H_c | i > \right|^2 \quad \frac{\delta(\omega_o^f - \omega_o^i)}{h} \tag{2}$$

where the wave functions are,

$$| \; f \; > \quad = \; | \; n + 1, \; n_{k_1} - 1, \; n_{k_2} - 1, \; n_{k_3} - 1 > \; \text{ and } \; | \; i \; > \quad =$$

$$| \; n, \; n_{k_1}, \; n_{k_2}, \; n_{k_3} >$$

The n_k label the vibrational states of the k th mode of the lattice and n the vibrational state of the molecule. The H_c represents the coupling between the lattice modes and the intra-molecular mode of the molecule and has been shown to be proportional to, (refs. 6, 7)

$$\gamma \; x U^3 \tag{3}$$

where γ is the fourth partial derivative of the potential seen by the molecule at the equilibrium position of the molecule, x is the normal coordinate of the molecular vibration and U is the displacement of the center of mass of the molecule. Lieberman, (refs. 6, 7), in the context of a different phenomenon, ultrasonic absorption in organic solids, has evaluated W_{10} for a three phonon process in a Debye solid.

The Debye solid assumes a Debye density of states.

The result is,

$$W_{10} = \frac{9k^3N^4}{16hm\ (4\pi M)^3}\ \frac{A^2\ T^3}{\nu\ \nu_d^7} \tag{4}$$

where M is the mass of the molecule and m is the mass of the atom vibrating in the molecule, ν_d is the Debye frequency of the lattice, ν is the internal mode frequency of the molecule, A is the coupling constant between the lattice mode and the molecular vibration, and T is the lattice temperature, in this case produced by the compression of the lattice due to the shock pulse. The probability of a transition per unit time from a level N to N + 1 is,

$$W_{N+1,N} = (N + 1)\ W_{10} \tag{5}$$

To obtain the reaction rate, the probability for the system to be excited from state O to L is required. Montroll and Shuler (ref. 5), have shown that this later can be treated as a one-dimensional random walk with an absorbing barrier with the probability per unit time that a walker will take a step from N to N+1 given by equations 4 and 5. The distribution of the molecules in the lattice over the vibrational states of the molecule is then time dependent. The mean first passage time, the average time for a walker to reach L+1 has been shown to be (ref. 5),

$$\bar{t} = \frac{1}{W_{10}}\ \sum_{1}^{L+1}\ \exp\ (J\theta)\ (\frac{1}{J} + \frac{1}{J+1}\ \text{--------}\ \frac{1}{L+1}) \tag{6}$$

where $\theta = h\ \nu/kT$. In the calculation of $\bar{t}$ it is assumed that all the oscillators are initially in the ground state, a reasonable assumption at room temperature. The model is particularly appropriate to the case of shock-induced temperature rise where the short duration of the temperature rise may not allow the population of the internal vibrational states of the molecule to be in equilibrium with the external lattice modes. The application of the model to the breaking of a bond of a diatomic molecule in a solid was first considered by Strenzwielk (ref. 8), who considered the case of a diatomic molecule in a one-dimensional lattice. However, the effect of shock compression on the lattice was not investigated.

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RESULTS

Slow thermal decomposition studies of RDX show that the dominant bond broken is the CN bond of the ring (ref. 3). Since W_{10} is zero unless $\nu CN = 3\nu_d$ then for this bond to be broken by a process involving transfer of lattice phonons to the molecule, the Debye frequency must be $\nu CN/3$. This places the Debye frequency of RDX at about 8.7×10^{12} s^{-1} which is not an unreasonable value. This model provides some general criteria for the occurrence of unimolecular reactions in solids. Those solids having molecular constituents with low intra-molecular vibrational frequencies and high Debye frequencies will be most susceptible to decomposition. This may possibly explain why NO_2 is not a major product of the slow thermal decomposition studies in that the stretch frequency of the N-N bond is too large to meet the Debye condition. However, because lattice frequencies and therefore, the Debye frequency increase with compression, it is possible that the $3\nu_d = \nu$ condition can be met at higher pressures of shock. The pressure at which the condition would be met can be estimated. Recent measurements of the effect of hydrostatic pressure on the lattice frequencies of RDX using Raman spectroscopy indicate that the Debye frequency would increase linearly with pressure having a slope of 0.6 cm^{-1}/Kb (ref. 9). Assuming shock compression causes the same change as hydrostatic pressure and assuming the dependence remains linear at higher pressures, it is estimated that the N-N stretch frequency would equal $3\nu_d$ at 80 Kb. Thus, above 80 Kb energy could be transferred to the N-N stretch vibration of the RDX molecule from the lattice. In view of the approximations involved in this estimate the absolute value of 80 Kb should not be taken too seriously. It is noteworthy, however, that a single crystal of RDX requires a shock pulse of peak value of 320 Kb to detonate (ref. 10).

To estimate the rate at which three lattice phonons can be trans-ferred to a specific internal vibration of a molecule as complex as RDX, it is necessary to make some severe approximations. It will be assumed that there is no coupling between the different vibrational modes of the molecule. This assumes that all the energy stays in the internal vibration to which it is transferred. It also allows the molecule to be treated as a heteronuclear diatomic molecule with each nuclear mass equal to the mass of the separated fragments that result from the breaking and the force constant equal to the force constant of the bond connecting the two fragments. Thus, for example, to calculate W_{10} for the N-N bond between NO_2 and the ring of RDX, the RDX is represented as a diatomic molecule with the two nuclei having masses equal to the masses of the two fragments.

In order to calculate W_{10} using equation 4 it is necessary to be able to estimate the temperature generated by the shock pulse. For a

single crystal of RDX the temperature rise can be estimated from the equation (ref. 11),

$$\Delta T_s = \frac{P^3}{\rho^3 C_p V_s{}^4} \qquad (7)$$

where C_p is the specific heat, V_s is the velocity of sound and the ρ is the density. The coupling constant A has been calculated for a number of different organic materials and is typically in the order of 10^{20} g cm^6/sec^2 (refs. 6, 7). Using this value W_{10} has been calculated for RDX for the CN bond and the N-N bond as a function of shock pressure taking into account the increase in the Debye frequency as a function of compression. The results are plotted in figure 1. The estimated relaxation times at all pressures is shorter than the duration of the shock pulses that are used to initiate RDX indicating that there is time for lattice energy to be transferred to the internal vibrations of the molecules of the solids. Taking the dissociation energy of the N-N bond as 3.0 eV, a value calculated from MO theory, the mean time for the N-N stretch vibration to be excited to N = 20 at which $D_e = (N+1)h\nu$ can be obtained from equation 6 (ref. 12). A similar calculation can be made for the C-N bond using an activation energy of 2.0 eV, the measured thermal activation energy (ref. 3). The estimated rates, the reciprocal of the mean time, are plotted as a function of pressure in figure 2. The values of the rates are in the order of reaction rates that have been measured in shock fronts by observing the build-up of gas behind the shock pulse, and are of the order needed to cause detonation (ref. 4). They are also in the order of magnitude of estimates of reaction rates obtained by extrapolating time to explosion versus temperature data to temperatures generated by shock pulses that cause initiation.

CONCLUSIONS

The possibility that the rate controlling step in shock initiation of solid explosives is the transfer of lattice phonons to internal vibrational modes of the molecules is examined. The rate at which three phonons can be transferred to the CN stretch and the NN stretch vibration of RDX is estimated. The relaxation time obtained for the transfer is such that the process could occur within the duration of a typical shock pulse used to detonate RDX. Because energy transfer can not occur unless $3\nu_d = \nu$ and because ν_d increases with compression of the lattice it is shown that molecular vibrations which can not be excited at atmospheric pressure may be excited by transfer of lattice phonons at higher pressures. The analysis does suggest the possibility that the transfer of lattice phonons may well be the rate controlling
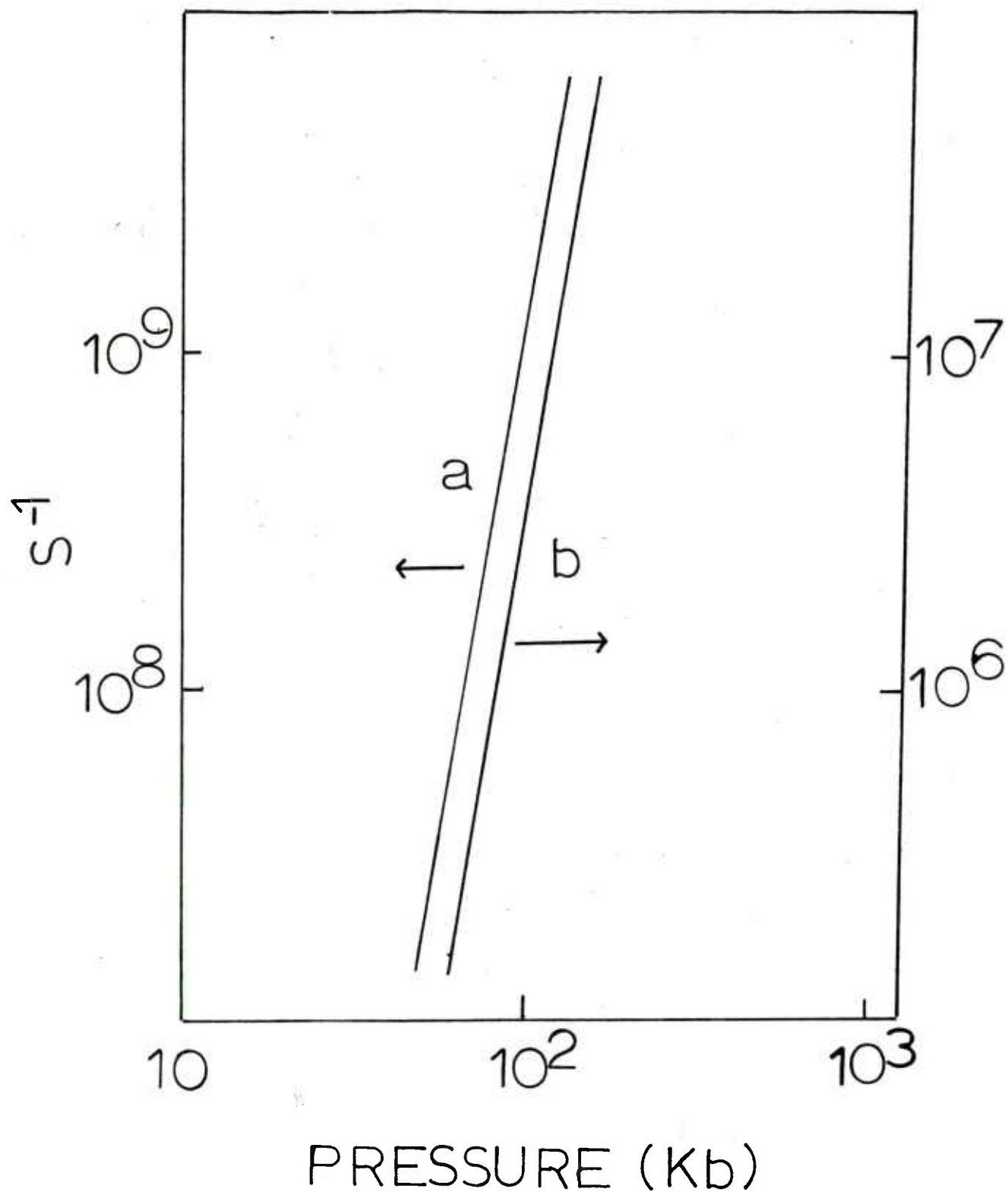
Figure 1. Calculated probability for $N = 0$ to $N = 1$
vibrational excitation of CN stretch (a)
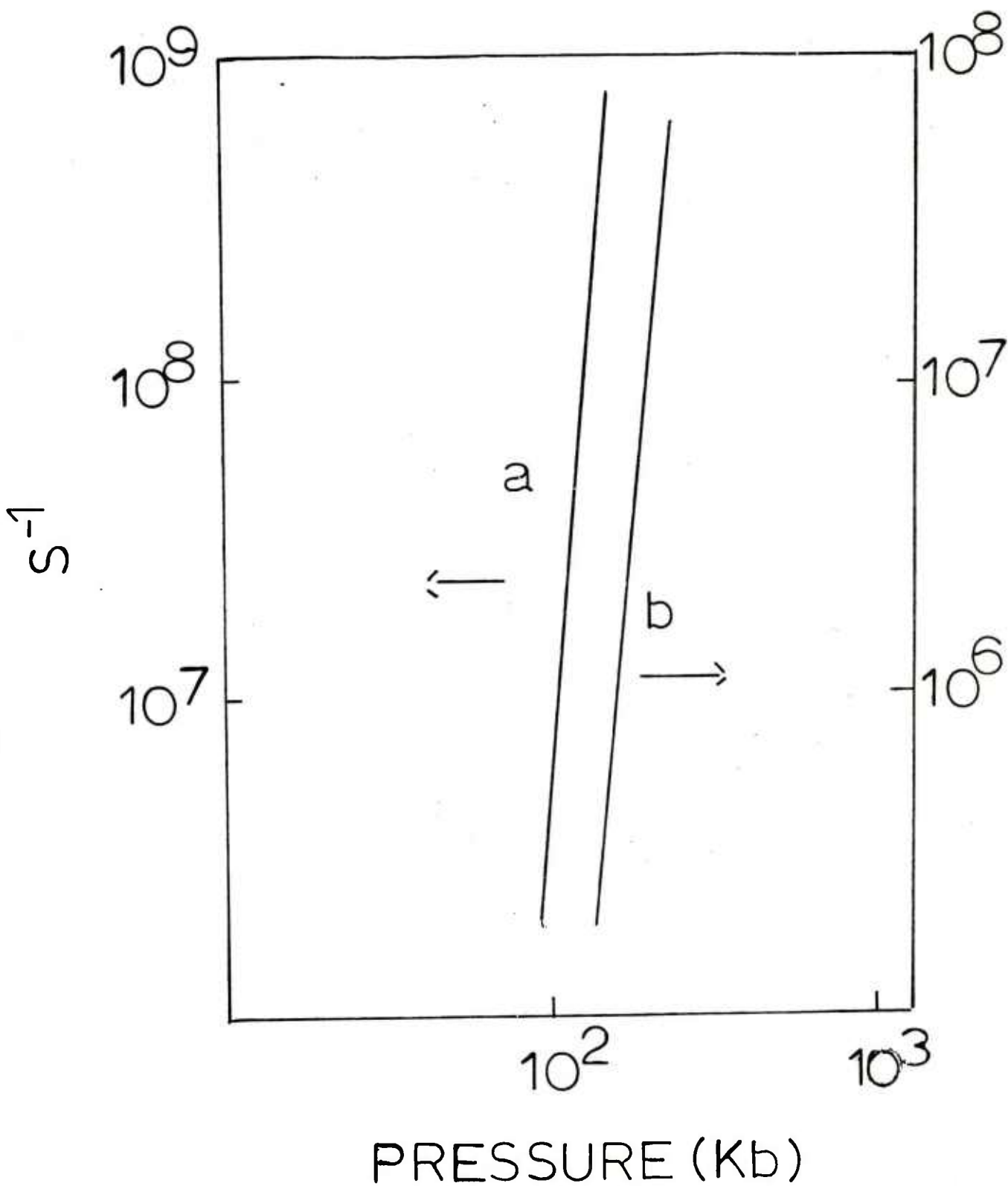and N – N stretch (b) as a function of peak
shock pulse pressure for RDX.

Figure 2. Calculated rates of reaction for breaking of CN
bond (a) and N – N bond (b) as a function of peak
shock pressure for RDX.

process in initiation. This possibility then suggests some character-
istics of organic explosive solids which may distinguish them from
non-explosives.

1. A strong coupling between lattice vibrations and internal
molecular vibrations.

2. The Debye frequency of the lattice must be greater than some
internal mode frequency at some pressure.

3. The Debye frequency may be more pressure dependent.

Generally by either calculation or experiment these characteristics
could be verified in explosive solids. The coupling between the
lattice modes and some internal mode of the molecules can be measured
by an acoustic resonance technique. Information about the Debye
frequency and its pressure dependence can be obtained from Raman
measurements of external modes at high pressures.

Although the rate at which a particular vibration of the molecule
can be excited to a dissociative state has been estimated, it is not
clear that this rate can be associated with a rate of unimolecular
bond breaking. This is because the coupling between the different
internal modes of the molecules has been neglected. Some of the
vibrationally excited energy of a specific vibration could be trans-
ferred to other vibrational modes of the molecule before the disso-
ciative state is achieved. The association of the calculated rates
with the rates of unimolecular bond breaking are valid only if the
time to excitation of the dissociative state is short compared with
the time for excited vibrational energy to be transferred to other
modes of vibration of the molecule. Recent studies of direct excita-
tion of specific vibrations of large molecules using tunable IR
pulsed lasers indicate that time for intra-molecular transfer are in
the order of 10^{-9} sec. Figure 2 indicates that the mean time to
reach a dissociative state in RDX depends strongly on shock pressure
and around 320 Kb, the shock pressure known to initiate a single
crystal of RDX, the calculated mean time is much shorter than 10^{-9}
sec. This suggests that a multivibrational excitation could lead to
high rate bond breaking at elevated pressures and that it may be
valid to associate the mean time to reach a dissociative state with
the rate of unimolecular bond breaking at high shock pressures.
There is thus another reason why the reactions of slow thermal decom-
position at lower temperatures and atmospheric pressures could be
different than the reaction of much higher temperatures and elevated
pressures. In the slow decomposition studies there is sufficient
time for the excitation energy of one bond to be distributed over
other vibrational modes of the molecule. In this case, the most
likely bond to be broken is the weakest bond of the molecule. In the

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high temperature and high pressure case the bond most likely to be broken is the bond most strongly coupled to the lattice vibrations. This work therefore, suggests that at high pressures and high temperatures the products produced from the unimolecular breakup of the molecules of the lattice may be quite different from those produced at atmospheric pressures and lower temperatures.

REFERENCES

1. F.J. Owens and J. Sharma, Chem. Phys.. Letters 61, 280 (1979).

2. F.J. Owens and J. Sharma J. Appl. Phys. (in press).

3. B. Suryanarayana, J.R. Autera, and R.J. Graybush, Proceedings Army Science Conference 2 (1968).

4. S.A. Sheffield, D.E. Mitchell, and D.R. Hays, Sixth Smyposium on Detonation, San Diego, CA (1976).

5. W.W. Montroll and K.E. Shuler, Adv. Chem. Phys. 1, 361 (1958).

6. L. Lieberman, Phys. Rev. 113 1052 (1959).

7. L. Lieberman in Physical Acoustics, Edited by P.W. Mason (Academic Press, 1966).

8. D.F. Strenzwilk, BRL Report 1724 (1974).

9. F.J. Owens and Z. Iqbal (unpublished).

10. B.G. Craig (unpublished).

11. P. Harris (Private communication).

12. M.J. Gallagher, M.S. Thesis, Texas A and M University, 1972.

13. M.E. Mack, R.L. Carman, J. Reintjes, and N. Bloembergen, Appl. Phys. Letters 16, 209 (1976).

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